

HOLOGRAPHIC RECORDING USING TWO-PHOTON INDUCED PHOTOPOLYMERIZATION

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ABSTRACT

Molecular excitation via the simultaneous absorption of two photons can lead to improved three-dimensional control of photochemical or photophysical processes due to the quadratic dependence of the absorption probability on the incident radiation intensity. This has led to the development of improved three-dimensional fluorescence imaging, optical data storage, and microfabrication. The latter of these involves the fabrication of three-dimensional structures using a spatial variation in the incident intensity within a photopolymerizable resin. In the past, the translation of the focal plane of a tightly focused laser beam was used to induce localized photopolymerization and fabrication of three-dimensional structures. Here we report the first successful demonstration of large area patterning via ultrafast holography-based two-photon polymerization of a commercially available optical resin and a large two-photon cross-section dye (AF380). This opens tremendous possibilities for the wide spread use of two-photon absorption for the three-dimensional control of photoinduced processes. Our eventual goal is to use this holographic process to duplicate biological structures that have been implicated as being important in infrared reception.

INTRODUCTION

Recently, we were the first to demonstrate holographic two-photon induced photopolymerization (H-TPIP) [1]. This work was complementary to previously published lithographic microfabrication using two-photon induced photopolymerization [2-4]; however, the addition of holographic techniques opened up enormous possibilities due to the ability to pattern large surface areas simultaneously. Increases in microfabrication complexity are made possible by using chromophores with increased two-photon cross-sections (σ) in conjunction with the confinement of the two-photon absorption to a volume on the order of λ_o^3 , where λ_o is the wavelength of incident radiation [5].

Traditional, one-photon induced polymerization has been well studied and has become an integral part of high precision processing such as microelectronic manufacturing, rapid prototyping via stereolithography, and MEMS manufacturing [6]. Two-photon induced polymerization has been studied to a lesser extent and offers strong promise as a method for the fabrication of 3D sub-micron structures including 3D optical data storage devices and photonic band-gap structures [7]. The initiation of both types of polymerization relies upon a photo-induced molecular excitation and subsequent generation of an initiating species. However, as with previous work on two-photon-based optical data storage [8], it was still necessary to sequentially scan a series of extremely short (100-150 fs), high peak power (<200-300 μ W) laser pulses in a tightly-focused single-beam geometry to cross the TPIP initiation threshold. H-TPIP

accomplishes this process without the need for a confocal single beam; thus, it represents a parallel form of photopolymer processing compared to the serial technique used previously.

Previously synthesized chromophores with large σ values allowed us to explore these alternative, non-focused laser geometries for TPIP microfabrication [9]. Specifically, we recorded diffraction gratings by combining two femtosecond pulses of near-infrared light. In the intervening months since first reporting this process, we have been studying the physics and behavior of this system. Particularly, we were intrigued by the hypothesis that the grating structure is actually formed by mass transport of monomer to polymer. This report updates the progress we have made in correlating polymer-grating thickness with laser exposure time. Additionally, we report on grating-formation kinetics measured in a real-time configuration by monitoring helium-neon laser transmission at 632 nanometers.

EXPERIMENTAL

Materials

AF380 represents one in a series of aromatic heterocyclic donor-acceptor chromophores consisting of π -electron donating and π -electron accepting moieties separated by a conjugated aromatic core. AF380 was selected on the basis of its large cross-section ($8.1 \times 10^{-21} \text{ cm}^4/\text{GW}$) and strong upconverted luminescence centered at 500 nm. NOA 72™ is commercially available free radical photopolymerizable thiol-ene optical adhesive which can be cured with light ranging from the 315 to 450 nm via photoinitiators with absorption peaks at 320, 365, and 420 nm [10].

Thin film fabrication

Thin films were fabricated by spin-coating a 0.4 wt.% blend of AF380 in NOA 72 onto polystyrene and glass slides using a Solitec 5110-C/T spincoater. To ensure solubility and dispersion of the AF380 within the NOA 72 matrix, the chromophore was dissolved in a small amount of benzene prior to blending (~5% benzene by volume in final solution). The NOA 72 was passed through a 2 μm filter prior to mixing with the chromophore. The final solution was filtered with a 0.45 μm syringe filter immediately prior to spin coating. Films were ~ 10 μm thick as determined by SEM cross-section.

SEM, AFM, & Optical Parameters

Electron microscopy was performed on a Leica 360FE scanning electron microscope. Samples were coated with a 10 Å layer of tungsten before imaging. AFM analysis was performed on a Digital Instruments MultiMode atomic force microscope operated in tapping mode. Optical microscopy was performed on a Nikon Optiphot microscope in transmission mode and captured using an integrated 35 mm camera.

Z-scan analysis

A standard Z-scan experiment was performed on the AF-380 chromophore in tetrahydrofuran (THF) to measure the two-photon absorption cross-section. Details of this experiment are described in the literature, therefore no description is given [11]. The experimental parameters for the scan were a beam waist of 130 μm , pulse width of 90 fs, pulse energies between 2–6 μJ , path lengths of 0.2, 0.5 and 1 cm, at a wavelength of 800 nm.

Optical Holographic Setup

The optical setup used to write the grating structures was a standard holographic configuration. A Ti:Sapphire femtosecond laser system with regenerative amplification was used to generate a bandwidth limited 90 fs, 950 μJ pulse centered at 800 nm at a repetition rate of 1 kHz. High intensity, low dispersion optics were used throughout the experimental arrangement. The spot size was reduced from 1 cm^2 to 4 mm^2 using a pair of thin lenses in a telescope arrangement, and the beam was split in two using a 70/30 ultrafast beam splitter. Each of the two beams was propagated along optical delay lines, one of which was a variable translation stage with a resolution of 8.3 fs/step. From the optical delay lines, the two beams were incident on the sample plane at an angle of 10° to the normal, subtending an angle of 20° between them. As the spatial extent of each pulse is approximately 30 μm , care must be taken to ensure accurate temporal and spatial overlap. To ensure temporal overlap, a KDP crystal was placed in the sample plane and the translation stage moved until the maximum of the second harmonic generation signal was measured. This process has the advantage of allowing us to also autocorrelate the pulse at the sample plane. By maximizing the temporal overlap, we were also forcing the two beams into coherence. In addition, both the KDP crystal and the sample holder were mounted on rails to ensure that the interaction plane was identical by sliding either one or the other into the overlapping beams. The energy of each pulse was attenuated using thin neutral density filters, and was measured at the sample plane using a calibrated power meter. The two beams had energies of 120 μJ and 150 μJ . Both the energy and beam size was chosen to give an appropriate intensity in order to initiate the two-photon photopolymerization, as described earlier. Exposure times were varied from 2 to 7 minutes.

RESULTS

Our initial transmission grating results are summarized in Figure 1 showing an AFM image of the grating structure. In this particular geometry, the grating exhibited a spacing of 3.8 μm and a surface modulation depth of 50 nm (peak to valley). Since our preliminary report, we have reduced the transmission grating spacing to around 800 nm, begun quantifying the system parameters for accurate modeling of complex patterns, and recorded several Bragg reflection gratings covering a square centimeter (to be reported elsewhere).

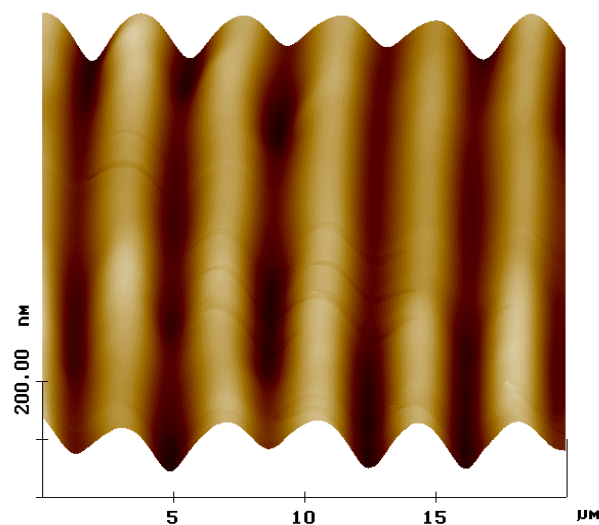


Figure 1 AFM image of transmission grating structure.

We have also demonstrated that the polymerization is truly a two-photon process by measuring the film thickness as a function of intensity. Shown in Figure 2 is a plot of polymer thickness versus pulse energy under identical conditions. As can be seen from the solid line, these data fit to a pure quadratic dependence as expected.

In order to make this technology useful for specific applications, it is necessary to understand the photophysical mechanisms responsible for the structure formation and then to combine this understanding with careful control over the phase and intensity profile of the short pulsed lasers needed to reach the intensities required. Therefore, in

beginning to quantify the mechanisms responsible for the formation of a grating, we have discovered a very rich and complicated chain of events, which will require further study. Presented in Figure 3 is a temporal measurement of the transmission of a helium-neon laser through the center region of a 10 micron film during the writing of a grating pattern. The relative mean intensity of the interference pattern is approximately half of what is typically used in order to slow down several of the processes visible. The first feature visible at zero time is an instantaneous drop in the transmission of the HeNe. This is believed to be due to excited state absorption (ESA) out of the initial two-photon excited state. A separate study on this process alone has been presented at a concurrent symposium [12]. The gradual increase in the transmission following the initial ESA can be attributed to a thermal relaxation of the viscosity of the film and a slow thinning of the film thickness in response to the thermal load. The ensuing large decrease in transmission may be the beginning formation of oligomers and the subsequent cross-linking to form polymer. Visual inspection of the film during this time shows a welling up of the material forming a lens type structure. The slow increase in the transmission at long times may be associated with the process

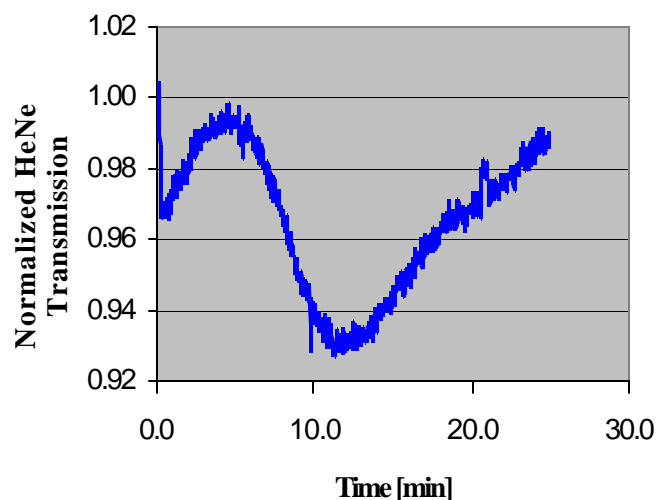


Figure 3 HeNe transmission versus time through a 10 micron film during a H-TPIP process.

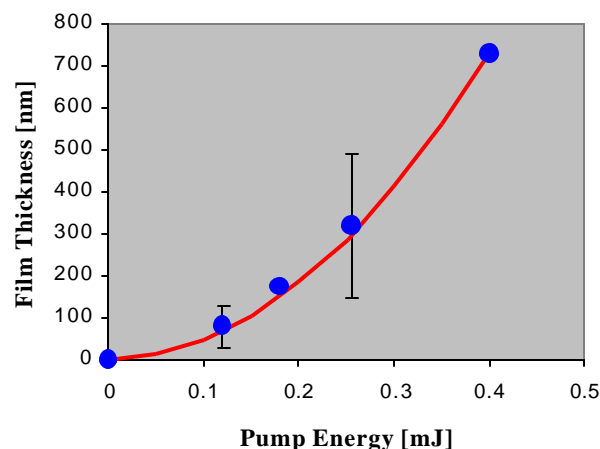


Figure 2 Film thickness as a function of pulse energy.

running out of material and slowly relaxing into a polymer film of uniform thickness. As the pulse energies are increased (and the corresponding intensities increased) the dip in transmission corresponding to polymer formation moves to the left in time, and eventually occurs nearly instantaneously. At these intensities, the polymer formation occurs much faster than the thermal relaxation making structure formation effectively thermally isolated as the exposure time can be reduced to essentially a few seconds or less. It should be noted that a thermal test of the system failed to produce any polymerization.

CONCLUSIONS

These results demonstrate that using a dye with a very large two-photon cross-section and a commercially available photopolymer, the process of two-photon-induced polymerization can be spatially controlled by using holographic techniques from a femtosecond laser. While preliminary results indicate that structure sizes on the order of nanometers are possible, there is still a great deal of work required to fully understand and model the holographic patterns with respect to the system kinetics. We believe that such parallel writing of two- and three-

dimensional structures will have a significant impact on current usage of TPIP technologies for data storage, MEMS, NEMS, and biotechnology.

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